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Thirteen new bi- or polycyclic vicinal exocyclic dimethylene hydrocarbons (10-22) have been synthesized and some of their spectral properties recorded. The generally most useful synthetic route to such compounds utilizes base-catalyzed double elimination from *trans*-1,2-bis(hydroxymethyl)alkyl *p*-toluenesulfonates as the final step in the production of the conjugated diene.

Treize nouveaux hydrocarbures (10-22), bi ou polycycliques, ayant des groupements diméthylènes exocycliques et vicinaux ont été synthétisés et quelques unes de leurs propriétés spectrales sont rapportées. La méthode de synthèse la plus efficace pour de tels composés consiste en une double élimination basocatalysée à partir des *trans* bis(hydroxyméthyl)-1,2 alkyl *p*-toluènesulfonates; ceci constitue l'étape finale en vue de la formation des diènes conjugués.

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Introduction

Interest in the chemistry of organic molecules containing proximal π -bonds is widespread in contemporary chemical literature (1). Perhaps the most interesting of this class of compounds are those in which the π -bonds are constrained in bi- and polycyclic hydrocarbons of known or predictable proximities by virtue of the fixed geometries of the ring systems involved, *e.g.* norbornadiene (2), barrelene (3), and bullvalene (4).

Most of the systematic work done, however, has been associated with endocyclic π -bonds. The synthesis of hydrocarbons of types 1 and 2 (where -X- represents any bridge) incorporating a vicinal exocyclic dimethylene bridge would allow a comparison of the effects of the possible mixing of the *cis*-diene π -orbitals with the endocyclic π -system of compounds 1 in the ground or first excited states with the situation as presented in compounds 2 where such mixing is not possible. Also, comparative chemistry (e.g. Diels-Alder additions) of 1 and 2 should reveal insights into the influence of ring size, state of hybridization, and -X-bridge geometric parameters on the transition states leading to the respective products. Such chemistry also generates many novel polycyclic systems, themselves potentially capable of further addition, thermal, or photochemical reactions. Accordingly, a synthetic program designed to provide a general high-yielding route to compounds of the type 1 and 2 was undertaken.



Of the compounds 3-22 below, 3-9 are known (5-8). The remainder (10-22) represent those of the many possible structures of (or related to) 1 and 2 which we have prepared to date. This paper describes their synthesis and offers general comments on the various methods available for the preparation of bridged vicinal dimethylene hydrocarbons.

Results and Discussion

The majority of the published syntheses of mono- and bicyclic vicinal exocyclic dimethylene hydrocarbons involves either acetate pyrolysis (route *i*, Scheme 1) (7, 9) or quaternary amine hydroxide (Hofmann elimination) pyrolysis (route *ii*, Scheme 1) (5) as the final diene producing step. The acetate route suffers from the high temperatures ($400-500^{\circ}$) necessary to effect elimination and cannot be considered when the possibility of retro-Diels-Alder reaction exists.

In this present work, route *ii* was modified to employ pyrolysis under vacuum of the bis-(dimethylamine-*N*-oxides) (Cope reaction (10)). The temperatures used were a little lower than in the Hofmann procedure, but it was found that with large scale preparations (up to 0.5 mol) uncontrolled decomposition of the *N*-oxide sometimes took place.

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SCHEME 1. General routes to vicinal exocyclic dimethylene hydrocarbons.

After the tosylation/base-catalyzed elimination sequence (route *iii*, Scheme 1) had been developed in this laboratory, the synthesis of 23(11) was published using exactly this method. This route proved to be the best in terms of overall yields, lack of hazard, and purity of product.

Compound 9 has been prepared using a modification of route *iii*, Scheme 1 (8) (as step h: sodium hydroxide/refluxing ethanol). However, the use of potassium *t*-butoxide in dimethyl sulfoxide at room temperature facilitated reaction and increased yields to *ca*. 95% from the *trans*-di-*p*-toluenesulfonate precursor.

Several other individual syntheses of vicinal

exocyclic dienes have been published (12) but these are not considered to be generally useful.

The ten hydrocarbons 3–8, 10, 11, 16, and 17 were all prepared via the Cope reaction modification as the final step of route *ii*, Scheme 1. The starting materials for all these compounds were the known, respective Diels–Alder adducts of fumaryl chloride and the cyclic diene necessary to construct the ring system. Thus, the corresponding intermediate bisamides, bisamines, and bisamine oxides all have *trans* stereochemistry.

The remaining ten hydrocarbons 9, 12-15, and 18-22 were all obtained from the di-*p*toluenesulfonate esters of the corresponding BUTLER AND SNOW: *π*-BOND SYSTEMS. I



bis-primary alcohols by treatment in dimethyl sulfoxide with potassium *t*-butoxide (route *iii*, Scheme 1). The starting compounds for the syntheses of hydrocarbons 9, 12–15, and 18 were again the fumaryl chloride adducts of the respective, necessary cyclic dienes. Catalytic hydrogenation reduced both double bonds of the diol intermediate from lithium aluminum hydride reduction of the cyclooctatetraene-fumaryl chloride adduct and thus furnished the necessary diol for compound 19.

The known 1,4-etheno-1,2,3,4-tetrahydro-

naphthalene-(*trans*)-2,3-dicarboxylic acid dimethyl ester **24** (13) was reduced in lithium aluminum hydride/tetrahydrofuran to provide the necessary diol intermediate for hydrocarbon **21**, and after catalytic reduction, that for hydrocarbon **22**. The advisability for having a *trans* disposition of the vicinal hydroxymethyl functions in these syntheses was revealed when attempted *p*-toluenesulfonation of the *cis*-diol **25** from lithium aluminum hydride reduction of the anthracene-maleic anhydride adduct produced the known cyclic ether **26** (14).

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Somewhat unexpectedly, the catalytic hydrogenation of the diol 27 reduced both double bonds, whereas the corresponding reduction of intermediate 28 (en route to 11) hydrogenated only the disubstituted olefin. The stereochemistry of 13 and its preceding intermediates are not known but they presumably are the *syn* isomers if reduction proceeded to the least hindered side of 27. The known *trans*-dimethyl ester 29 (15) provided the required intermediates for hydrocarbon 20 via the route *iii*, Scheme 1 sequence.

The physical, analytical, and spectroscopic data for the 13 new hydrocarbons (10-22) supporting the structural assignments are collected along with the unpublished spectra of the seven known compounds 3-9 in Tables 1 and 2. The exocyclic methylene absorption in the p.m.r. spectra all occur as two singlets or very narrow doublets between δ 5.25 and 4.60 p.p.m. and represent the "inside" and the "outside" vinyl protons. From the observed anisotropic effects of the olefinic bond (16) it is likely that

the "inside" proton would be the more deshielded. The chemical shift difference in these two protons varies regularly with the size of the -X- bridge in the series 4, 6, and 8 and inversely to the carbon-carbon double bond stretching frequency in the i.r. spectra suggesting a systematic influence of geometrical parameters on these spectroscopic measurements. The u.v. spectra of those hydrocarbons not containing any aromatic rings easily divide into the two structure types 1 and 2 and clearly indicate the *cisoid* conformation of the diene moiety (17). We are investigating these geometric-spectroscopic relationships further as well as the Diels-Alder reactivity and electrocyclic chemistry of this series of related hydrocarbons.

Experimental

All melting points are uncorrected. The i.r. spectra were determined on a Unicam SP1000 spectrophotometer as liquid films or as KBr discs. The p.m.r. spectra were recorded on Varian HA100 or A60 instruments in carbon tetrachloride or deuteriochloroform using tetramethylsilane as the internal standard. Mass spectra were taken at 70 eV using a

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TABLE 1. Hydrocarbons (3-22), physical, analytical, i.r., and u.v. data

Melting or boiling Compound (°C or °C	Malting point		Observed	Analytical data (%))		Ultraviolet spectra
	or boiling point (°C or °C/mm)	Molec- ular) formula	parent ion <i>m/e</i>	Calculated		Found		Strong infrared [‡]	
				С	Н	С	Н	(cm ⁻¹)	$m\mu$ (log ε)
3	142/760	C ₉ H ₁₀	118	_			_	670, 756, 784, 876, 1312, 1646, 2986, 3076	206 (3.88), 222 (3.86) s, 228.5 (3.92), 240 (3.95) b
4	67/50	C ₉ H ₁₂	120		_			877, 1113, 1636, 2870, 2966, 3080	205 (3.35), 241 (3.92) s, 248 (3.95)
5	68/12	C ₁₀ H ₁₂	132	_		—	_	677, 741, 875, 1610, 2865, 2955, 3055	205 (3.92), 214 (3.50) s, 219.5 (3.56), 226 (3.63) s, 246 (3.91), 252 (3.91)
6	93/50	$C_{10}H_{14}$	134	_	_		_	880, 1455, 1614, 2858, 2935, 3078	205 (3.31), 247 (3.88), 252 (3.88)
7	88/20	C ₁₁ H ₁₄	146	_			_	701, 881, 1441, 1606, 2857, 2930, 3040	206 (3.70), 246.5 (3.83) b, 252 (3.82)
8	103/30	$C_{11}H_{16}$	148	_		—	—	884, 1453, 1602, 2862, 2930, 3082	205 (3.29) s, 247 (3.87) b
9	157-157.5*	C ₁₈ H ₁₄	230			-	_	720, 727, 738, 758, 875, 889, 1624, 2965, 3020, 3070	208 (4.17), 240.5 (3.54) s, 252 (3.47), 261 (3.37) s, 268.5 (3.31) s, 276 (3.18)
10	74.5 75.5	$C_{12}H_{14}$	158	91.08	8.92	91.31	8.91	672, 780, 868, 1646, 1653, 2930, 2982, 3010, 3070	205.5 (3.88), 230 (4.04) s, 246 (4.11) b
11	66.5-67	$C_{12}H_{16}$	160	89.94	10.06	90.02	10.10	737, 809, 881, 1620, 1639, 2860, 2980, 3085	204.5 (3.67), 250 (4.07) b
12	95-96	C ₂₂ H ₁₈	282	93.58	6.42	93.34	6.40	690, 734, 744, 790, 874, 883, 1595, 1641, 2985, 3010, 3025, 3035	206.5 (4.45), 225 (4.23) b, 267 (4.10) b
13	103.5104.5	$C_{22}H_{22}$	286	92.26	7.74	92.19	7.77	697, 870, 880, 1585, 1595, 1633, 2960, 3020, 3050, 3080	207 (4.28), 222 (4.10), 241 (3.86) s, 249 (3.91), 259 (3.74) s
14	†	C ₁₁ H ₁₂	144	91.61	8.39	91.50	8.61	671, 777, 877, 1005, 1308, 1428, 1658, 2985, 3075	205 (3.93), 229 (3.95) s, 241.5 (3.98)
15	†	$C_{11}H_{14}$	146	90.35	9.65	90.54	9.41	804, 876, 1003, 1636, 2872, 2968, 3076	205 (3.38), 242.5 (3.93) s, 247.5 (3.97), 257 (3.77) s
16	†	$C_{11}H_{12}$	144	91.61	8.39	91.63	8.20	681, 739, 811, 837, 880, 1628, 2955, 3020, 3050, 3080	205 (3.77), 225 (3.74) s, 242 (3.91), 247 (3.90)
17	t	C ₁₁ H ₁₄	146	90.35	9.65	90.11	9.73	835, 880, 1620, 2875, 2948, 3008, 3079	206 (3.43) s, 243.5 (3.91), 249.5 (3.92)
18	t	$C_{12}H_{12}$	156	92.26	7.74	92.31	7.89	679, 727, 778, 878, 1297, 1615, 2950, 3050	206 (3.72), 243.5 (3.91), 249 (3.90)
19	15†	C12H16	160	89.94	10.06	89.68	10.20	882, 1616, 2950, 3080	207 (3.33), 247.5 (3.91), 253 (3.91) s
20	45†§	$C_{12}H_{12}$	156	92.26	7.74	91.99	7.89	680, 780, 882, 1266, 1601, 1619, 2980, 3075	205 (3.40), 254 (3.77), 262 (3.74) s
21	47–48	$C_{14}H_{12}$	180	93.29	6.71	93.48	6.77	660, 708, 745, 765, 809, 882, 1614, 2980, 3075	208.5 (4.50), 234 (4.34) s, 243 (4.32), 277 (3.74)
22	93.5–94	C ₁₄ H ₁₄	182	92.26	7.74	92.46	7.67	707, 763, 883, 1608, 2865, 2950, 3020, 3075	208.5 (4.17), 251.5 (4.03), 263.5 (3.84) s, 271.5 (3.48)

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*Literature m.p. 151-153° (8). †Sample transferred under vacuum (0.01 mm); bath temperature 40-120° as appropriate. ‡Infrared spectra taken as liquid films and KBr discs. §Vacuum transfer at 80°/0.01 mm caused partial thermal reversion to 18. || Taken in ethanol solution; s, shoulder; b, broad.

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	Vicinal	Exomethylene			
	vinyl	vinyl			
Compound	-C=C- H H	$=c <_{H}^{H} \ddagger$		Bridgehead C—H	Other proton assignments
3	6.10(2H)	5.06(2H)	4.86 (2H)	3.22 (2H)	1,47–1,78 (2H)§
4		5.02 (2H)	4.73 (2H)	2.76 (2H)	1.16-1.80(6H)
5	6.17(2H)	5.03 (2H)	4.67 (2H)	3.12 (2H)	1.22 - 1.72(4H)§
6		5.14 (2H)	4.62 (2H)	2.26 (2H)	1.58 (8H)§
7	6.02 (2H)	5.25 (2H)	4.68 (2H)	2.92 (2H)	1.36-1.80 (6H)§
8		5.21 (2H)	4.62 (2H)	2.56 (2H)	1.42-1.82 (10H)§
9	—	5.16 (2H)	5.01 (2H)	4.71 (2H)	6.92-7.24 (8H) aromatic
10	6.22 (2H)	4.98 (2H)	4.81 (2H)	3.63 (2H)	1.52 (6H) gem dimethyl
11	_	4.95 (2H)	4.67 (2H)	3.12 (2H)	1.61 (6H) gem dimethyl; 1.35-1.78 (4H)§
12	6.35 (2H)	5.12(2H)	4.91 (2H)	3.75 (2H)	6.96-7.30 (10H) aromatic
13	_	4.98 (2H)	4.64 (2H)	2.39 (2H)	7.02-7.24 (10H) aromatic; 3.60 (1H) benzylic; 1.28-2.04 (5H)§
14	6.16(2H)	5.07 (2H)	4.80 (2H)	2.57 (2H)	0.22-0.59 (4H) cyclopropyl
15	_	5.04 (2H)	4.66 (2H)	1.96 (2H)	1.32-1.95 (4H)§; $0.28-0.50$ (4H) cyclopropyl
16	5.71 (2H)	5.09(2H)	4.73 (2H)	3.22 (2H)	0.96 (2H), 0.12-0.32 (2H) cyclopropyl
17		5.21 (2H)	4.69 (2H)	2.48 (2H)	0.06-1.02 (4H) cyclopropyl; 1.18-1.50 (4H)§
18	{5.89 (2H) {5.83 (2H)	5.16 (2H)	4.75 (2H)	3.07 (2H)	2.72 (2H) cyclobutenyl
19 20		5.15 (2H) 5.22 (2H)	4.60 (2H) 4.71 (2H)	2.39 (2H)	1.99-2.26 and 1.33-1.59 (10H)§ 3.02-3.43 (8H) bridgehead and cyclobutyl
21	6.47 (2H)	5.07 (2H)	4.87 (2H)	4.35 (2H)	6.90-7.15 (4H) aromatic
22	_	5.12 (2H)	4.81 (2H)	3.56 (2H)	7.03 (4H) aromatic; 1.40–1.92 (4H)§

TABLE 2. The 100 MHz p.m.r. data for hydrocarbons 3-22*†

* δ -Value determined in CCl₄ solution using TMS as internal standard.

†Unless otherwise shown, the centers of multiplets are indicated. ‡Singlets or narrow doublets ($J \le 1.0$ Hz).

§Protons in saturated bridge or bridges.

Hitachi-Perkin Elmer RMU-6E instrument. Microanalyses were obtained from A. B. Gygli, Toronto.

Starting Materials - Diels-Alder Adducts

(anti)-Tricyclo[$3.2.2.0^{2.4}$]non-8-ene-(*trans*)-6,7-dicarbonyl chloride (18); (anti)-tricyclo[$4.2.2.0^{2.5}$]deca-3,9-diene-(*trans*)-7,8-dicarbonyl chloride (19); 7-isopropylidenebicyclo[2.2.1]hept-5-ene-(*trans*)-2,3-dicarbonyl chloride (20); 7-diphenyl-methylenebicyclo[2.2.1]hept-5-ene-(*trans*)-2,3-dicarbonyl chloride (21); 1,4-etheno-1,2,3,4-tetrahydronaphthalene-(*trans*)-2,3-dicarboxylic acid dimethyl ester (24) (13); penta-cyclo[$4.2.2.0^{2.5}.0^{3.8}.0^{4.7}$]decane-(*trans*)-9,10-dicarboxylic acid dimethyl ester (29) (15).

Spiro[cyclopropane-1,7'-[5]norbornene]-(trans)-2',3'dicarbonyl Chloride

Fumaryl chloride (36 g) in dry ether (50 ml) was added dropwise over 1 h to an ice-cooled solution of spiro[2.4]hepta-4,6-diene (22) (19 g) in dry ether (250 ml). The resulting solution was evaporated to a yellow-green oil which showed p.m.r. absorptions (CCl₄) at δ 6.18, m (2H); 3.93, m (1H); 3.16, d (J = 5.5 Hz) (1H); 2.90, m (2H); and 0.41 p.p.m., s (4H) consistent with the adduct structure. This oily dichloride was directly reduced to the corresponding diol without further identification (see below).

Preparation of Bis(N,N-dimethylamides)

The diacid chloride (0.1 mol) was dissolved in dry diethyl ether (70 ml) and slowly dropped into an ice-cooled solution of dimethylamine (0.5 mol) in dry diethyl ether (200 ml).

After allowing the reaction mixture to come to room temperature, the dimethylammonium chloride was filtered off, washed with ether, and the filtrate evaporated to afford the crude bisamide. This was dissolved in benzene (100 ml) and passed through a bed of neutral alumina (Woelm: activity grade 1; 20×2.5 cm). A further 400 ml of benzene were passed through the column and the total eluate evaporated to leave the pure amides. The yields were almost quantitative. The analytical samples were either recrystal-lized from ether or sublimed.

The following new compounds were prepared by this method. (*anti*)-Tricyclo[$3.2.2.0^{2.4}$]non-8-ene-(*trans*)-6,7-bis-(*N*,*N*-dimethylcarboxamide), m.p. 122–123.5°.

Anal. Calcd. for $C_{15}H_{22}N_2O_2$: C, 68.67; H, 8.45; N, 10.68. Found : C, 68.42; H, 8.58; N, 10.46.

7-Isopropylidenebicyclo[2.2.1]hept-5-ene-(*trans*)-2,3-bis-(*N*,*N*-dimethylcarboxamide), m.p. 93.5-94.5°.

Anal. Calcd. for $C_{16}H_{24}N_2O_2$: C, 69.53; H, 8.75; N, 10.14. Found: C, 69.20; H, 8.59; N, 10.28.

The above two bisamides were subjected to catalytic hydrogenation in methanol using 10% palladium-oncharcoal as catalyst. After 1 mol of hydrogen had been absorbed, the catalyst was filtered off and the solvent removed under vacuum. The remaining dihydrobisamides were essentially pure. Analytical samples were recrystallized from ether. (*anti*)-Tricyclo[3.2.2.0^{2,4}]nonane-(*trans*)-6,7-bis-(*N*,*N*-dimethylcarboxamide), m.p. 135-136.5°.

Anal. Calcd. for C₁₅H₂₄N₂O₂: C, 68.15; H, 9.15; N, 10.60. Found: C, 68.14; H, 9.33; N, 10.34.

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7-Isopropylidenebicyclo[2.2.1]heptane-(*trans*)-2,3-bis-(*N*,*N*-dimethylcarboxamide), m.p. 114-115.5°.

Anal. Calcd. for $C_{16}H_{26}N_2O_2$: C, 69.03; H, 9.41; N, 10.06. Found: C, 69.32; H, 9.37; N, 9.68.

Preparation of the Bisamines

The above amides were individually reduced in diethyl ether using lithium aluminum hydride (1.2 mol/mol) bisamide) by refluxing for 10 h. After this time a volume of 20% KOH solution (equal to the weight in grams of bisamide taken) was added dropwise, followed by an equal volume of water. After stirring for 2 h, this mixture was filtered, the precipitate washed well with ether, and the filtrate evaporated to give the crude bisamines as yellow oils. The yields were variable (50-85%) and these products were oxidized directly to the bisamine oxides.

Oxidation of Bisamines

The above bisamines were individually taken up in methanol (500 ml/mol) and 30% H₂O₂ (60 ml) added in 5 ml batches over 1 h. Further 60 ml portions of 30% H₂O₂ were added after 2 and after 6 h and the mixture allowed to stand overnight. The excess H₂O₂ was decomposed by the cautious addition of a small quantity of platinum black, and when no more oxygen was seen to be forming, the mixture was filtered and evaporated under vacuum to give the crude bis(amine-N-oxides) as viscous oils. They were directly pyrolyzed without further purification.

Pyrolysis of Bis(amine-N-oxides)

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The bis(amine-N-oxides) (0.1-0.5 mol), contained in a 11 round bottom flask connected to a liquid air cooled vacuum trap, were separately heated under vacuum (0.1 mm) using a free flame. Decomposition began from about 80° and heating was continued until all the contents of the flask had decomposed. Considerable charring occurred in most cases. The contents of the trap were extracted with petrol ether (30-60°) and washed three times with water. The combined extracts were dried over anhydrous magnesium sulfate, filtered, and evaporated at 25° (water pump pressure). The residue was taken up in petrol (10 ml) and passed through a short column of alumina $(10 \times 1.0 \text{ cm})$ using further solvent to wash the column. The total eluate was evaporated and the residue either vacuum transferred or recrystallized from methanol to afford the pure hydrocarbons (see Tables 1 and 2). The yields were 20-40% based on the bisamine taken.

Preparation of Diols and Di-p-toluenesulfonates

The diacid chloride (0.1 mol) in dry diethyl ether (70 ml) was slowly dropped into a stirred suspension of lithium aluminum hydride (0.2 mol) in 1:1 dry diethyl ether/dry tetrahydrofuran (300 ml). After the initial reaction had subsided, the mixture was subjected to reflux for 16 h and the excess hydride decomposed by the addition of a volume of 20% aqueous KOH solution (equal to the weight in grams of dichloride taken) followed by an equal volume of water. After stirring a further 2 h at room temperature, the precipitate was filtered, washed well with ether, and the total filtrate evaporated to afford the crude diol. In some of these reductions, the diol remained complexed to the precipitated alumina and was extracted therefrom with ethanol. If the diol crystallized, analytical samples were prepared by recrystallization from benzene or carbon tetrachloride. If it

did not crystallize, it was converted to the di-p-toluenesulfonate directly. The yields varied from 50-80%.

In the case of the *trans*-dimethyl esters 24 and 29, the above reduction was carried out in dry tetrahydrofuran rather than the mixed ether solvent.

The following pure diols were prepared by this method. They all exhibited strong hydroxyl absorption near 3350 cm⁻¹ in their i.r. spectra. The di-*p*-toluenesulfonates were prepared by the standard method (*p*-toluenesulfonyl chloride/pyridine, 0 °C, overnight).

trans-7,8-Bis(hydroxymethyl)-(*anti*)-tricyclo[4.2.2.0^{2,5}]-deca-3,9-diene, m.p. 93-93.5°.

Anal. Calcd. for C₁₂H₁₆O₂: C, 74.97; H, 8.39. Found: C, 74.80; H, 8.13.

Di-p-toluenesulfonate, m.p. 159-160° (methanol).

Anal. Calcd. for $C_{26}H_{28}O_6S_2$: C, 62.38; H, 5.64. Found : C, 62.42; H, 5.73.

trans-2,3-Bis(hydroxymethyl)-1,4-etheno-1,2,3,4-tetrahydronaphthalene, m.p. 142–143°.

Anal. Calcd. for C₁₄H₁₆O₂: C, 77.75; H, 7.46. Found: C, 77.57; H, 7.54.

Di-p-toluenesulfonate, m.p. 133-134° (methanol).

Anal. Calcd. for $C_{28}H_{28}O_6S_2$: C, 64.10; H, 5.38. Found: C, 64.12; H, 5.46.

The following diols were prepared by the above route but analytical samples were not secured. All showed consistent i.r. and p.m.r. spectra for the structures indicated:

trans-2',3'-Bis(hydroxymethyl)spiro[cyclopropane-1,7'-[5]norbornene]. Di-*p*-toluenesulfonate, m.p. 120.5-121.5° (methanol).

Anal. Calcd. for $C_{25}H_{28}O_6S_2$: C, 61.45; H, 5.78. Found: C, 61.51; H, 5.88.

trans-9,10-Bis(hydroxymethyl)pentacyclo[$4.2.2.0^{2.5}.0^{3.8}$ - $.0^{4,7}$]decane. Di-*p*-toluenesulfonate, m.p. 177–178° (methanol).

Anal. Calcd. for $C_{26}H_{28}O_6S_2$: C, 62.38; H, 5.64. Found: C, 62.55; H, 5.85.

trans-2,3-Bis(hydroxymethyl)-7-diphenylmethylenebicyclo[2.2.1]hept-5-ene. Di-*p*-toluenesulfonate failed to crystallize.

Catalytic Reduction of the Diols

The diols were reduced in methanol using 10% Pd-on-C as catalyst and isolated in the usual way. If they did not crystallize they were directly converted to the *p*-toluenesulfonates as above. The following pure diols and di-*p*-toluenesulfonates were obtained. All showed consistent i.r. and p.m.r. data for the structures indicated.

trans-7,8-Bis(hydroxymethyl)-(*anti*)-tricyclo[$4.2.2.0^{2.5}$]-decane, m.p. $82-83^{\circ}$.

Anal. Calcd. for C₁₂H₂₀O₂: C, 73.43; H, 10.27. Found: C, 73.41; H, 9.97.

Di-p-toluenesulfonate, m.p. 178.5-179.5° (methanol).

Anal. Calcd. for $C_{20}H_{32}O_6S_2$: C, 61.88; H, 6.39. Found: C, 61.75; H, 6.51.

trans-2,3-Bis(hydroxymethyl)-1,4-ethano-1,2,3,4-tetrahydronaphthalene, m.p. 129–130°.

Anal. Calcd. for C₁₄H₁₈O₂: C, 77.03; H, 8.31. Found: C, 76.96; H, 8.31.

Di-p-toluenesulfonate, m.p. 132.5-133° (methanol).

Anal. Calcd. for $C_{28}H_{30}O_6S_2$: C, 63.85; H, 5.74. Found: C, 63.93; H, 5.77.

trans-2,3-Bis(hydroxymethyl)-7-(diphenylmethyl)bicyclo-

[2.2.1]heptane di-p-toluenesulfonate, m.p. 110-110.5° (methanol).

Anal. Calcd. for C₃₆H₃₈O₆S₂: C, 68.54; H, 6.07. Found: C, 68.73; H, 6.27.

trans-2',3'-Bis(hydroxymethyl)spiro[cyclopropane-1,7'di-p-toluenesulfonate, m.p. norbornane] _110_111° (methanol)

Anal. Calcd. for C₂₅H₃₀O₆S₂: C, 61.20; H, 6.16. Found: C, 61.35; H, 6.08.

General p-Toluenesulfonate Elimination Procedure

To the di-p-toluenesulfonate (0.01 mol) dissolved in dimethyl sulfoxide (60 ml) was added powdered potassium t-butoxide (0.025 mol). The mixture darkened rapidly to deep green-brown and was stirred at room temperature for 5 h. The mixture was poured onto ice-water (200 g) and extracted with petroleum ether (30-60°) (4 \times 30 ml). The combined extracts were washed with saturated sodium chloride solution $(3 \times 100 \text{ ml})$ to remove the dimethyl sulfoxide, dried over anhydrous magnesium sulfate, and evaporated to yield the crude hydrocarbon. The yields varied from 80-95%. The pure hydrocarbons were secured by chromatography in petroleum ether (30-60°) over alumina (Woelm: activity grade 1; 20×1 cm column), evaporation of the solvent under vacuum and sublimation or vacuum transfer at 40-140° and 0.01 mm depending on the melting or boiling point of the sample. The physical, analytical, and spectroscopic data are collected in Tables 1 and 2.

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